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# On the Transjointing Reactions of Jointed Compounds

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CITATION:

Oda, Ryohei ...[et al]. On the Transjointing Reactions of Jointed Compounds. Bulletin of the Institute for Chemical Research, Kyoto University 1953, 31(5): 378-380

ISSUE DATE:

1953-09-30

URL:

<http://hdl.handle.net/2433/75355>

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In the reaction of paraffin, as given in Table 1, it was found that the reaction did not occur in mild conditions as in the lower hydrocarbons, and that the phosphorous content of the products was increased as the molar ratios of phosphoroustrichloride and of oxygen to the paraffin were increased. Similar result was obtained with liquid paraffin, as given in Table 2.

Table 2.

|                 | Original-<br>compound<br>(g) | PCl <sub>3</sub><br>(g) | CCl <sub>4</sub><br>(g) | O <sub>2</sub><br>(hr) | Temp.<br>(C) | P-contents<br>(%) |
|-----------------|------------------------------|-------------------------|-------------------------|------------------------|--------------|-------------------|
| Liquid paraffin | 22                           | 52.5                    | 0                       | 12                     | 67~70        | 1.64              |
| Stearic acid    | 21.4                         | 74.7                    | 0                       | 12                     | 70~75        | 4.17              |

Then, with stearic acid and cetylalcohol some experiments were performed to see the influence of carboxyl group upon the reactivity of the hydrocarbon chain.

One of the data is given in Table 2.

The results show that the carboxyl group activates the paraffin chain to some degree. For the reaction of cetylalcohol the result is not given because the analysis was confused by the formation of cetyl-alcoholmonophosphoric acid ester.

The isolation of the paraffin phosphonic acid in pure state from the reaction mixture was so difficult that the products which has a purity higher than 50 % could not be obtained, but the product was found to be the expected paraffin phosphonic acid by means of the formation of alkali salts.

In the case of liquid paraffin, phosphonyldichloride was treated with glycerin in the presence of pyridin and the corresponding diglyceride was obtained; the phosphor content of this diglyceride was analysed and found to be 5,11 % (calculated value 5,48 %).

Conclusion.

The authors have acertained that this synthetic method can be applied to higher hydrocarbons in proper conditions, although the yield of the phosphonyldichloride is not so high and the purification procedure is not easy.

## 11. On the Transjointing Reactions of Jointed Compounds

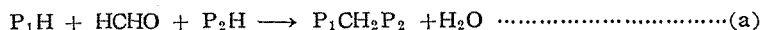
Ryohei ODA and Mototeru NOMURA

(Oda Laboratory)

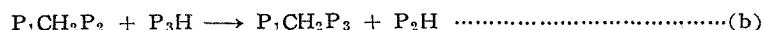
### Introduction

The condensation of two passive components (P<sub>1</sub>H and P<sub>2</sub>H) with formaldehyde

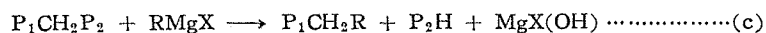
was named a joint reaction.



And many examples are already known, in which a third passive component ( $P_3H$ ) reacts with this jointed compound displacing the  $P_2H$  as shown in scheme (b). The authors would name this reaction a "transjointing".

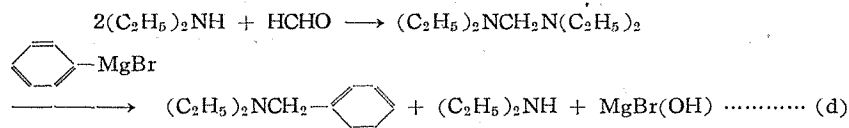


The authors have performed some experiments upon this transjointing, especially using the Grignard reagent as  $P_3H$ . We can find no examples about transjointing with Grignard reagent, though it is expected to proceed as scheme (c).



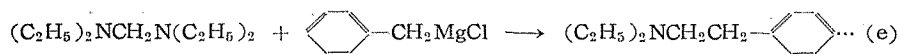
(A) Transjointing reactions of tetraethyl methylene diamine (I) with Grignard reagent

(I) was prepared by jointing two molecules of diethyl amine with formaldehyde and this compound reacted with phenyl magnesium bromide. As the result diethyl benzyl amine was obtained in 26 % yield as shown in scheme (d). Another diethyl-amino group could not be replaced, even if two moles of Grignard reagent to one mole of (I) were used.



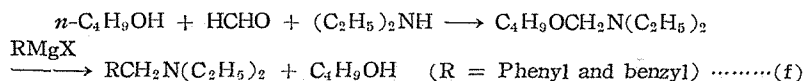
This reaction was so mild that the reaction mixture was warmed on a water bath for 4 hrs. to complete the reaction.



(I) and benzyl magnesium chloride reacted similarly and diethyl  $\beta$ -phenethyl amine was obtained in 15.3 % yield.



(B) Transjointing reaction of diethylaminomethyl *n*-butyl ether (II) with Grignard reagent

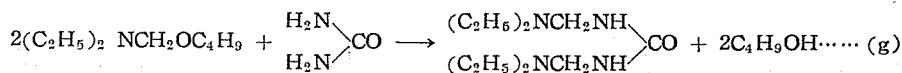
(II) was prepared by jointing diethyl amine and *n*-butyl alcohol with formaldehyde. This jointed compound is asymmetric as to the methylene group, and therefore two possibilities of transjointing can be considered. The experiments of transjointing of (II) with phenyl magnesium bromide and benzylmagnesium chloride showed that only butoxy group was substituted with phenyl and benzyl group respectively, as shown in the following scheme :



In this reaction the product was the same amine as that of experiment (A). But (II) is more reactive than (I) with Grignard reagent so that the vessel must be cooled with ice during the reaction. The yields of amine were 67.5 % (in the case of -MgBr) and 89.4 % (in the case of -CH<sub>2</sub>MgCl) respectively, thus much higher than that in experiment (A).

(C) Transjointing of (II) with urea

As the butoxy group of (II) was found to be very reactive we studied the trans-jointing of (II) with urea. The ether (II) (0.2 mole) was added to 0.1 mole of urea and warmed on a water bath for 20 mins. By vacuum distillation butyl alcohol was removed and NN'-bis-diethylaminomethyl urea (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCH<sub>2</sub>NHCONHCH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> remained as the residue. The yield of butyl alcohol was about 90 % of calcd. value. Thus, it is evident that reaction proceeded as follows :



## 12. Reaction of Ketene with Silk

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The refined silk turns gradually yellow or brown in color. The brownization is thought to be due to the presence of free amino group and especially the hydroxyl group of tyrosine in silk fibroin. A protection of these free groups by acetylation may prevent the brownization.

Some refined silk samples (yarn and cloth), therefore, were treated with gaseous ketene without any catalyst under the same conditions as free phenol and aniline were easily acetylated.

On exposure test to sunlight or ultra-violet rays, however, it was found that the ketene treatment did not improve the property of silk.

Some mechanical properties of silk seemed to be improved somewhat by an appropriate ketene-treatment. The experimental conditions and results are summarized in Tables 1. and 2.

Table 1. Action of ketene on phenol and aniline in ether and at room temperature.

| Substance     | Ketene* (gas) | Product                    |
|---------------|---------------|----------------------------|
| Phenol (47g)  | 21g           | Phenylacetate 52g. (77%)   |
| Aniline (23g) | 6.854g        | Acetanilide 20.488g. (93%) |

\* Ketene was estimated by the NaOH method.